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PRELIMINARY INVESTIGATION
OF EFFECT OF ENVIRONMENTAL
FACTORS ON SALT STRESS CORROSION
CRACKING OF Ti-8A1-1Mo-1V
AT ELEVATED TEMPERATURES

by David N. Braski

Langley Research Center
Langley Station, Hampton, Va.

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

A preliminary experimental investigation was made on the effect of oxygen, moisture, pressure, surface condition, and salt composition on the salt stress corrosion cracking of Ti-8Al-1Mo-1V titanium-alloy sheet (duplex annealed) at 550° F (561° K) and 600° F (589° K). The results showed that both a reduction in the oxygen content and pressure reduced stress corrosion cracking. Thin surface oxide films and moisture in the ranges investigated had little or no effect on the amount of stress corrosion damage. NaCl caused more damage than ASTM salt (six parts NaCl to one part $MgCl_2$, by weight). Moist chlorine produced severe stress corrosion cracking. $TiCl_2$ appeared to be one of the main corrosion products.

INTRODUCTION

At present, one of the leading skin materials being considered for use on a Mach 3 supersonic transport is the titanium alloy Ti-8Al-1Mo-1V. A number of investigators, however, have found that when this alloy is coated with salt it is very susceptible to stress corrosion cracking at elevated temperatures. (See refs. 1 and 2.) Before a decision can be made as to whether stress corrosion cracking would present a serious problem for a supersonic transport under actual operating conditions, many questions concerning the mechanism of this phenomenon and the environmental conditions must be answered.

In this preliminary investigation, the effect of oxygen, moist chlorine, moisture, pressure, surface condition, and salt composition on the stress corrosion cracking of Ti-8Al-1Mo-1V (duplex annealed) sheet material was studied. Self-stressed specimens were salt coated and sealed in glass tubes with various environments and then exposed at 550° F (561° K) and 600° F (589° K) for times up to 3000 hours. Some salt-coated specimens were exposed to air under the ambient conditions in the oven. After various exposures, the specimens were tested in compression to measure quantitatively the amount of stress corrosion damage that occurred in each environment. Photomicrographs of representative stress corrosion cracks were taken. X-ray diffraction techniques were used in

an attempt to identify the corrosion products formed with Ti-8Al-1Mo-1V and NaCl at 1000° F (811° K). This report presents the experimental procedure, data, and results for the investigation.

The units used for the physical quantities appearing in this paper are given in both the U.S. customary units and the International System of Units (SI) (ref. 3). The relationship between these two systems of units is shown in appendix A.

MATERIAL AND SPECIMENS

All specimens were fabricated from 0.050-inch- (0.127-cm-) thick Ti-8Al-1Mo-1V sheet in the duplex-annealed condition. The following information of chemical composition, heat treatment, and typical tensile properties of this material was supplied by the producer.

Chemical composition:

Element	C	Fe	N	Al	V	Mo	H_2
Weight percent	0.026	0.11	0.011	7.9	1.0	1.1	0.003 to 0.006

Heat treatment:
   Hold at 1450° F (1061° K) for 8 hours; furnace cool
   Reheat to 1450° F (1061° K) for 1/4 hour; air cool

Typical tensile properties:
   Yield strength . . . . 136 ksi (938 MN/m²)
   Tensile strength . . . . 152 ksi (1048 MN m²)
   Elongation . . . . 13 percent

The self-stressed corrosion specimens were designed to obtain maximum outer fiber stresses of 100 ksi (689 MN/m²). All specimens were fabricated in the longitudinal grain direction as follows:

   (1) Cut and machine 4- by 1/4-inch (10.16- by 0.64-cm) strips (fig. 1(a))

   (2) Bend ends of each strip to bend angle of approximately 12° (fig. 1(b))

   (3) Clean the strips chemically (see section entitled "PROCEDURE")

   (4) Place two cleaned strips together, clamp the ends, and spotweld (fig. 1(c)). Handle all specimens carefully with clean white golves throughout this operation to prevent any contamination.

The magnitude of the outer fiber stresses depends upon the radius of curvature, the thickness of the sheet strip, and Young's modulus for the material at the exposure temperature. As long as the strips are stressed below the elastic limit, the distance D (see fig. 1(c)) between the inner faces of the

2

strips can be determined for a given maximum fiber stress from the following geometrical and stress-strain relationship:
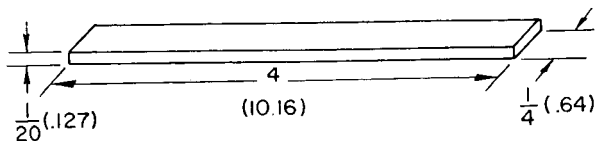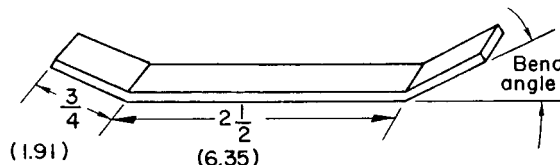
$$D = 2R - \sqrt{4R^2 - c^2}$$
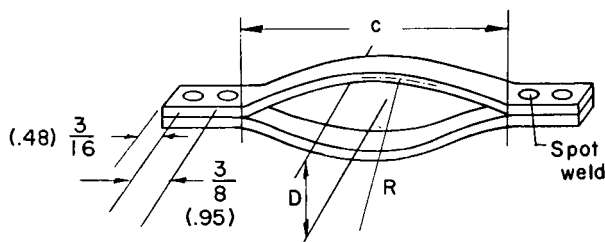
where

$$R = \frac{tE}{2\sigma}$$

and

R radius of curvature, in. (cm)

c chord length or distance between bent-up ends, in. (cm)

t strip thickness, in. (cm)

E Young's modulus at test temperature, 17.5×10^3 ksi $(120.6 \times 10^3$ MN/m$^2)$

σ tensile or compressive stress, ksi (MN/m^2)

(a) Machined strip.

(b) Strip with ends bent.

(c) Completed specimen.

Figure 1.- Construction of self-stressed specimen. Dimensions are given in inches and parenthetically in centimeters.

PROCEDURE

A list of the stress corrosion experiments performed in this investigation is shown in table I. The specimen conditions, environment specifications, and exposure data are shown for each experiment. The following paragraphs give detailed explanations of cleaning, surface preparation, salt coating, encapsulation, and exposure, as well as procedures for compression testing the specimens after exposure and examining them metallographically. The procedure used for X-ray diffraction analysis of corrosion products is also given.

Cleaning

It was necessary to have a clean surface to obtain uniform salt coatings and to insure the elimination of all extraneous elements that could influence the stress corrosion process. The specimens were cleaned prior to fabrication to remove all grease and foreign matter as follows:

(1) Clean with acetone and cloth

3

TABLE I.- SUMMARY OF STRESS CORROSIO

Experiment	Number of specimens	Surface condition	Salt coating	Environment	Environment specifications
1	16	As received	NaCl	O_2	Bottled O_2, 99.7 percent purity, 3 ppm H_2O
2	16	As received	NaCl	N_2	Bottled N_2 98.998 percent minimum purity Percent maximum, by weight: O_2 0.002 H_2 1.000 H_2O 0.0007
3	16	As received	NaCl	Moist air	Atmospheric air, dewpoint 60° F (289° K)
4	12	As received	NaCl	Dry air	Atmospheric air, dried with $CuSO_4$, Dewpoint -40° F (233° K)
5	12	As received	Uncoated	Cl_2	Generated by heating MnO_2 and HCl; Cl_2 was bubbled through water before entering capsule
6	16	As received	NaCl	Oven atmosphere	Still air
7	16	As received	NaCl	Vacuum	
8	12	As received	NaCl	Vacuum	
9	16	Polished	NaCl	Oven atmosphere	Still air
10	16	Gold anodized	NaCl	Oven atmosphere	Still air
11	16	Blue anodized	NaCl	Oven atmosphere	Still air
12	12	As received	NaCl	Vacuum	
13	12	Polished	NaCl	Vacuum	
14	16	As received	ASTM salt	Oven atmosphere	Still air

[a]Equivalent values expressed in SI units are shown in parentheses.

Encapsulation temperature		Encapsulation pressure (a)	Exposure temperature		Exposure times, hours
°F	°K		°F	°K	
78	299	Atmospheric (101 kN/m²)	550	561	650, 1000, 2000, 3000
78	299	Atmospheric (101 kN/m²)	550	561	650, 1000, 2000, 3000
78	299	Atmospheric (101 kN/m²)	550	561	650, 1000, 2000, 3000
78	299	Atmospheric (101 kN/m²)	550	561	1000, 2000, 3000
78	299	Atmospheric (101 kN/m²)	550	561	500, 1000, 2000
		Atmospheric (101 kN/m²)	550	561	500, 1000, 2000, 3000
550	561	34 mm Hg (4.55 kN/m²)	550	561	240, 500, 1000, 3000
78	299	3×10^{-5} mm Hg (4.0 mN/m²)	550	561	1000, 2000, 3000
			550	561	500, 1000, 2000, 3000
			550	561	500, 1000, 2000, 3000
			550	561	500, 1000, 2000, 3000
600	589	3×10^{-5} mm Hg (4.0 mN/m²)	600	589	500, 1000, 1500
600	589	3×10^{-5} mm Hg (4.0 mN/m²)	600	589	500, 1000, 1500
			550	561	500, 1000, 2000, 3000

(2) Immerse in NaOH base cleaner (6 ounces NaOH per gallon of water (45 kg/m^3)) at 200° F (366° K) for 10 minutes (600 seconds)

(3) Rinse in hot water

(4) Dip in 20 percent nitric acid solution for 30 seconds

(5) Rinse thoroughly in tap water and dry

Specimen Surface Preparation

After fabrication, the Ti-8Al-1Mo-1V specimens were prepared with four different surface conditions: as received, polished, blue anodized, and gold anodized. The as-received surfaces were essentially in the same condition that the material was received from the producer except that the cleaning procedure described in the previous paragraph was used to remove all grease and foreign matter. The polished specimens were produced by hand polishing the outer surfaces in the longitudinal direction with No. 600 grit silicon carbide paper under water. The polishing operation was followed by degreasing with acetone. The oxide layer on the as-received and polished surfaces was in the range of 100 to 200 angstroms and 12 to 16 angstroms thick, respectively (interpreted from data in ref. 4). Gold and blue anodized surfaces were produced electrolytically as outlined in appendix B. The gold and blue anodized surfaces had oxide thicknesses of 300 and 600 angstroms, respectively, as determined by their interference colors (derived from data in ref. 5).

Salt Coating

Reagent-grade sodium chloride was applied by dipping the specimens into a boiling, supersaturated salt solution, and then drying them in an oven at 250° F (394° K). This procedure was repeated as many times as needed to produce a salt coating approximately 0.005 inch (0.013 cm) thick over the surfaces of the specimen. Salt was removed from the ends of the specimens to prevent corrosion from developing at or near the spot welds. One group of specimens was coated in the same manner by using ASTM salt (six parts NaCl to one part $MgCl_2$, by weight).

Encapsulation of Specimens

In order to study the effects of different amounts of oxygen and moisture on the stress corrosion of Ti-8Al-1Mo-1V, salt-coated specimens were encapsulated in glass tubes with oxygen, nitrogen, and air with dewpoints of -40° F (233° K) and 60° F (289° K). A group of uncoated specimens was also encapsulated in moist chlorine gas to determine the manner in which this gas reacts with Ti-8Al-1Mo-1V and the resultant corrosion products. Figure 2(a) is a sketch of the type of capsule used for encapsulation with a gas. Other

6

salt-coated specimens were encap-
sulated under reduced pressures of
34 (4.55 kN/m^2) and 3 × 10^{-5} mm Hg
(4.0 mN/m^2) to study the effects
of pressure. (See fig. 2(b).)
Figure 2(c) represents a sealed
capsule ready for exposure. The
detailed procedure used for encap-
sulating specimens is given in
appendix C.

(a) Encapsulating with a gas.

(b) Encapsulating under reduced pressure.

Exposure

The specimens were exposed at
550° F (561° K) in electric ovens
for times up to 3000 hours. One
group of specimens, encapsulated
under reduced pressure, was
exposed at 600° F (589° K) for
times up to 1500 hours. The
specimens and specimen capsules

(c) Completed capsule ready for exposure.

Figure 2.- Encapsulation of specimens.

were removed from the ovens at regular intervals for examination and testing.
Three specimens were not exposed to elevated temperature but were tested at
room temperature to establish a control standard.

Mechanical Test

After exposure, the salt coatings were removed with a water rinse and
specimens were tested in compression at room temperature by utilizing the fix-
tures shown in figure 3. A special fixture was used to aline the upper and
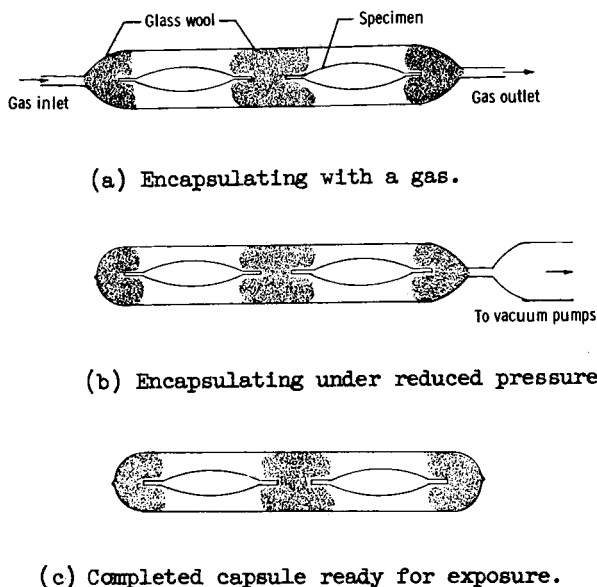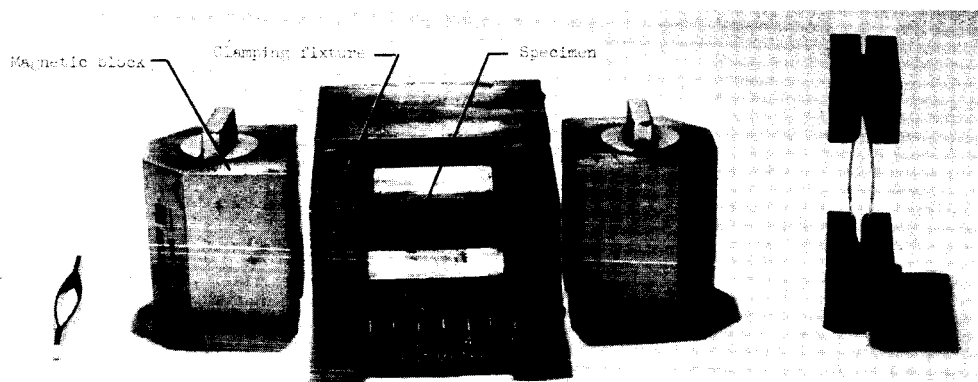

(a) Specimen.   (b) Alinement fixtures.

L-64-7025.1
(c) Specimen with upper and
lower clamping fixtures.

Figure 3.- Specimen, alinement fixtures, and clamping fixtures.

lower clamps with the specimen (fig. 3(b)). These clamping fixtures were used to support the specimen vertically in the hydraulic testing machine (fig. 3(c)). Load was applied at a rate of 200 pounds per minute (15 N/s) and recorded autographically against head displacement. The head displacement, which is equivalent to specimen shortening, was measured by a deflectometer consisting of an aluminum-alloy cantilever beam instrumented with strain gages at the base of the beam.

Metallurgical Examination

Metallurgical samples were cut from the curved portions of tested specimens remote from the fracture zone, where the effects of bending due to the compression test were negligible. The samples were edge mounted, polished, and then etched with a solution of 97 percent H_2O, 2 percent HNO_3, and 1 percent HF, by volume. The samples were examined and photomicrographs of representative stress corrosion cracks were obtained by using a metallograph.

Identification of Corrosion Products

A brief X-ray diffraction study was undertaken in an attempt to identify the corrosion products associated with the salt stress corrosion mechanism in Ti-8Al-1Mo-1V. Salt stress corrosion at $550°$ F ($561°$ K) and $600°$ F ($589°$ K) produced so small an amount of corrosion product that identification by conventional X-ray diffraction techniques was impossible. To produce a substantial amount of corrosion product it was necessary to expose a salt-coated, 1- by 2-inch (2.54- by 5.08-cm) coupon of Ti-8Al-1Mo-1V at $1000°$ F ($811°$ K) for 100 hours. After exposure, the coupon was placed immediately in the X-ray diffractometer and scanned at $2°$ per minute. Copper K_α radiation with a power setting of 40 kV and 16 mA was used, with a $3°$ beam slit, medium resolution collimator, $0.2°$ detection slit, and nickel filter. This procedure was repeated with a second salt-coated coupon and also an uncoated coupon to verify the results.

RESULTS AND DISCUSSION

The effects of the various environments on the stress corrosion cracking in Ti-8Al-1Mo-1V were evaluated by the compression tests. Typical specimen configurations before and after compression testing are illustrated in figure 4. Specimens with no stress corrosion cracks could be compressed approximately 1.6 inches (4.1 cm) before fracture occurred at the bend (fig. 4(b)). Specimens with stress corrosion cracks fractured after relatively small amounts of shortening (fig. 4(c)). It was shown in reference 2 that the greater the maximum crack penetration, the smaller the amount of shortening needed to produce fracture. The following paragraphs are a discussion of the effects of different variables and enviroments on the stress corrosion cracking of Ti-8Al-1Mo-1V specimens stressed at 100 ksi (689 MN/m^2). The results are shown graphically with specimen shortening at fracture, determined from the compression tests,

Before test   After test

(a) Original   (b) No stress corro-   (c) Stress corro-
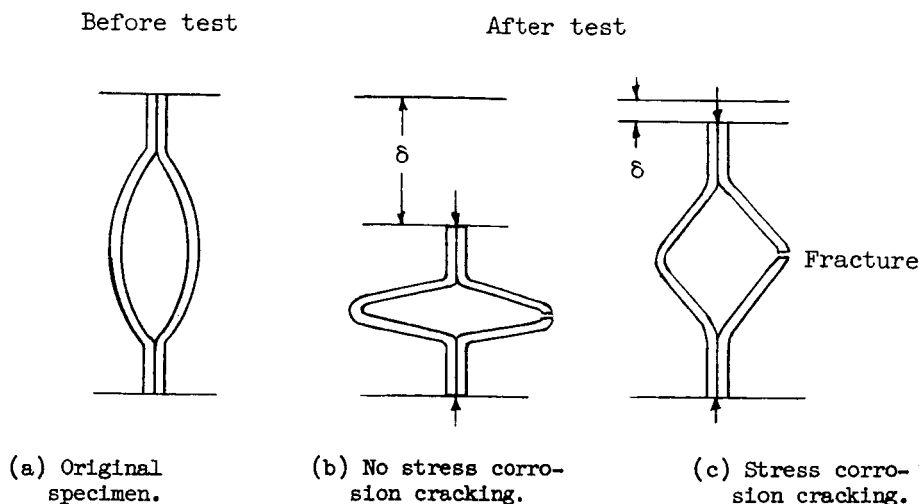   specimen.   sion cracking.   sion cracking.

Figure 4.- Specimen configuration before and after room-
temperature compression test. δ represents shortening.

plotted as a function of exposure time. Limiting curves, faired through the lowest data points, are used to represent the maximum stress corrosion damage that occurred under the test conditions.

Effect of Oxygen and Moisture

It is recognized that oxygen is an important factor in the stress corrosion mechanism in titanium alloys (see refs. 6, 7, and 8), but the effect of the amount and form of oxygen has not been established. The results of compression tests on specimens encapsulated in nitrogen, oxygen, moist air, and dry air (experiments 1, 2, 3, and 4 in table I), are shown in figure 5. These four environments contain three levels of gaseous oxygen: 0.002 percent (nitrogen), 100 percent, and 21 percent (air), by volume. The results show that the 100 percent oxygen, moist air, and dry air produced approximately the same amount of stress corrosion damage, whereas exposure in the nitrogen, with only 0.002 percent oxygen, produced less than one-half as much damage in the same time period.

Figure 5 shows that specimens encapsulated in air with dewpoints of -40° F (233° K) and 60° F (289° K) displayed almost the same values of shortening with exposures up to 3000 hours. Therefore, moisture in this dewpoint range had little effect on stress corrosion cracking.

It is obvious from these results that oxygen is one of the main elements involved in the salt stress corrosion cracking of Ti-8Al-1Mo-1V. The author believes that with very small volumes of oxygen, the TiO_2 and/or TiO on the titanium surface also play an important role in the stress corrosion reactions. Kochka and Peterson, in reference 6, demonstrated that reacting TiO_2, NACl, and titanium together at elevated temperature without oxygen will produce the familiar blue-gray stress corrosion product. It appears, therefore, that the
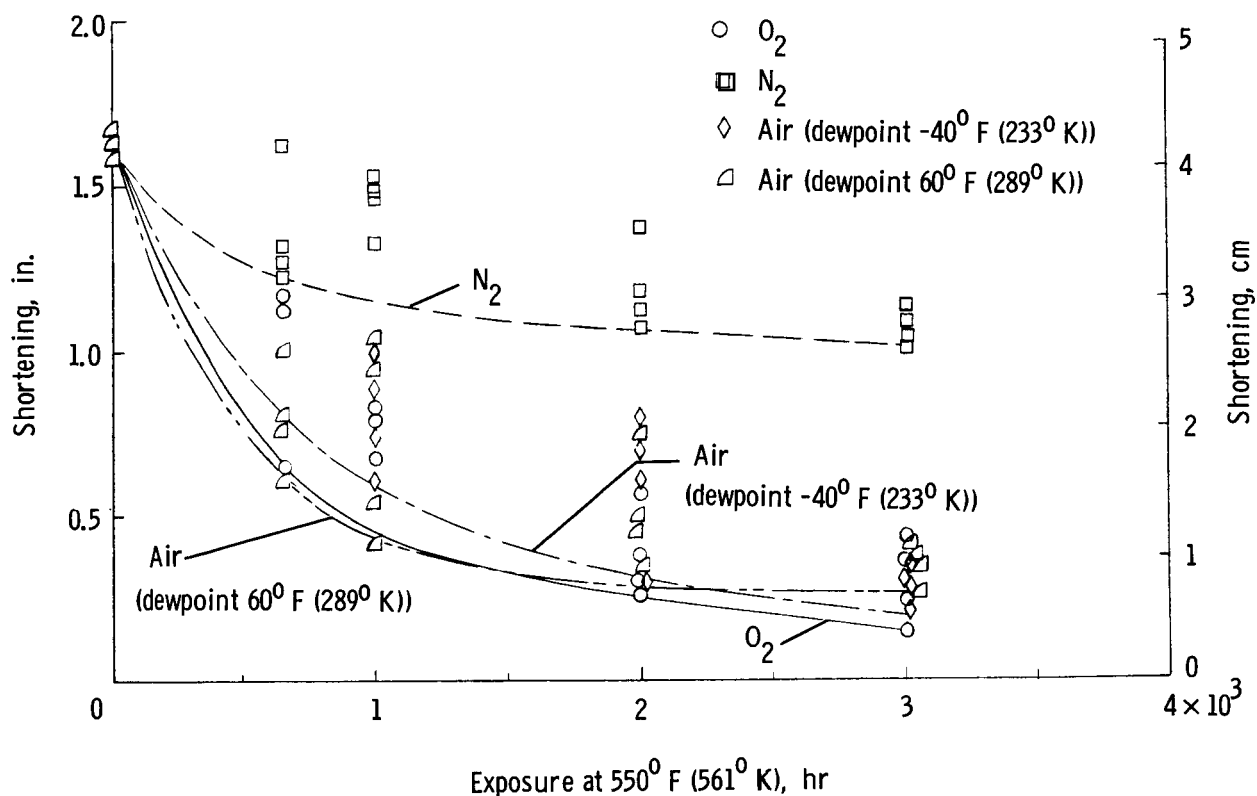
Figure 5.- Effect of oxygen, nitrogen, dry air, and moist air on shortening of
Ti-8Al-1Mo-1V specimens after exposure at 550° F (561° K).

general equations describing the corrosion reactions should include the case where the amount of gaseous oxygen present is essentially nil.

Figures 6 and 7 show photomicrographs of intergranular stress corrosion cracks in salt-coated specimens encapsulated in oxygen and in nitrogen and exposed for 3000 hours at 550° F (561° K). The cracks produced in the oxygen environment were more numerous and penetrated deeper into the base material than those produced in nitrogen.

Effect of Moist Chlorine

Moist chlorine gas was found to produce extremely severe stress corrosion in uncoated Ti-8Al-1Mo-1V at 550° F (561° K) (experiment 5 in table I). All of the specimens failed completely as a result of stress corrosion cracking before the 500-hour exposure time was reached. In every case, failure occurred at the intersection of the straight and bent portions of the specimens before removal from the oven. Figure 8 shows a photomicrograph of a stress corrosion failure area at one such intersection. Note the small intergranular cracks branching off of the main crack where failure occurred. The cracks were most numerous in

the vicinity of fracture and only a few
were observed on the center portions of
the specimen.

The specimens were covered with a
dark purple corrosion product whose
color and solubility properties in water
are similar to those of $TiCl_3$. Attempts
to identify the products by X-ray dif-
fraction failed as they were extremely
hygroscopic. This experiment has shown
that moist chlorine causes severe stress
corrosion cracking, with a $TiCl_3$ corro-
sion product, but it does not provide
any clue as to the role of moisture in
combination with chlorine.

Effect of Pressure

The effect of atmospheric
($101kN/m^2$), 34 mm Hg (4.53 kN/m^2), and
3×10^{-5} (4.0 mN/m^2) pressure on the
salt stress corrosion cracking of
Ti-8Al-1Mo-1V (experiments 6, 7, and 8
in table I) is shown in figure 9. (The
pressure of 34 mm Hg simulates the
static pressure at an altitude of
70,000 feet (about 21,000 m), the
approximate cruising altitude for a
supersonic transport.) Note that, as
the pressure is reduced, the damage due
to stress corrosion cracking is also
reduced. This result generally agrees
with tests reported in reference 8 on
Ti-5Al-2.5Sn at various reduced pres-
sures down to 1 micron (133 mN/m^2)
exposed at $800°$ F ($700°$ K) for 1 hour.
The reduction of stress corrosion
cracking with lower pressure can be
explained by the decreased amounts of
oxygen available to the reaction.

Effect of Surface Condition

Initially, the polished, as-
received, gold-anodized, and blue-
anodized specimens had oxide layers 12
to 16, 100 to 200, 300, and 600 ang-
stroms thick, respectively
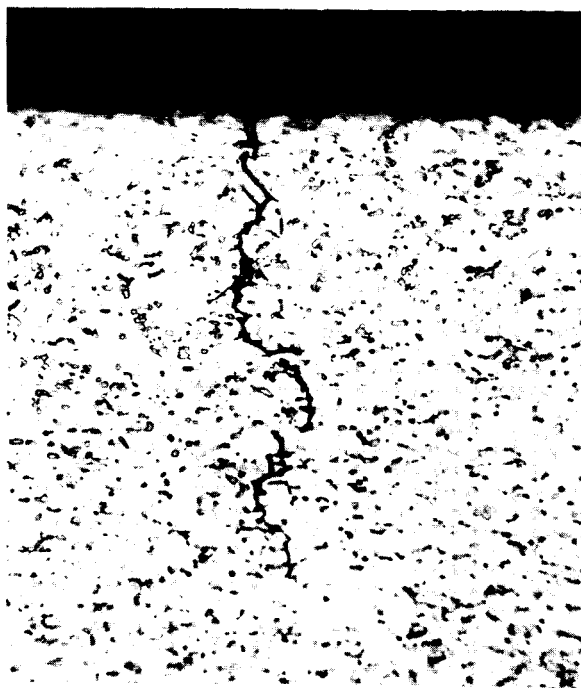
L-64-8381
Figure 6.- Stress corrosion crack in
Ti-8Al-1Mo-1V specimen encapsulated
in oxygen for 3000 hours at 550° F
(561° K). ×500.
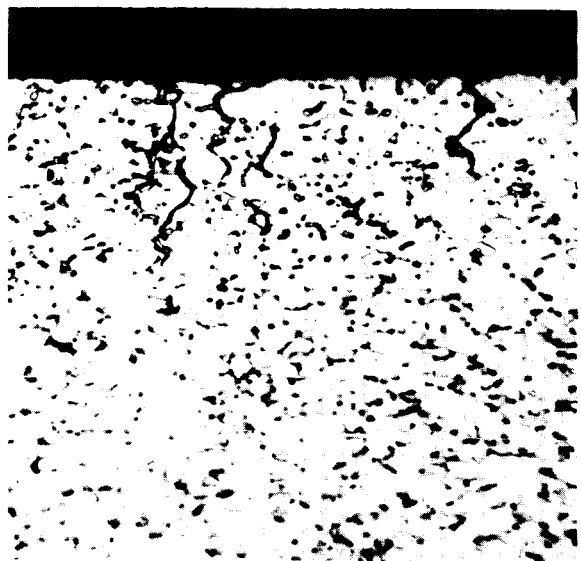
L-64-8382
Figure 7.- Stress corrosion cracks in
Ti-8Al-1Mo-1V specimen encapsulated
in nitrogen for 3000 hours at
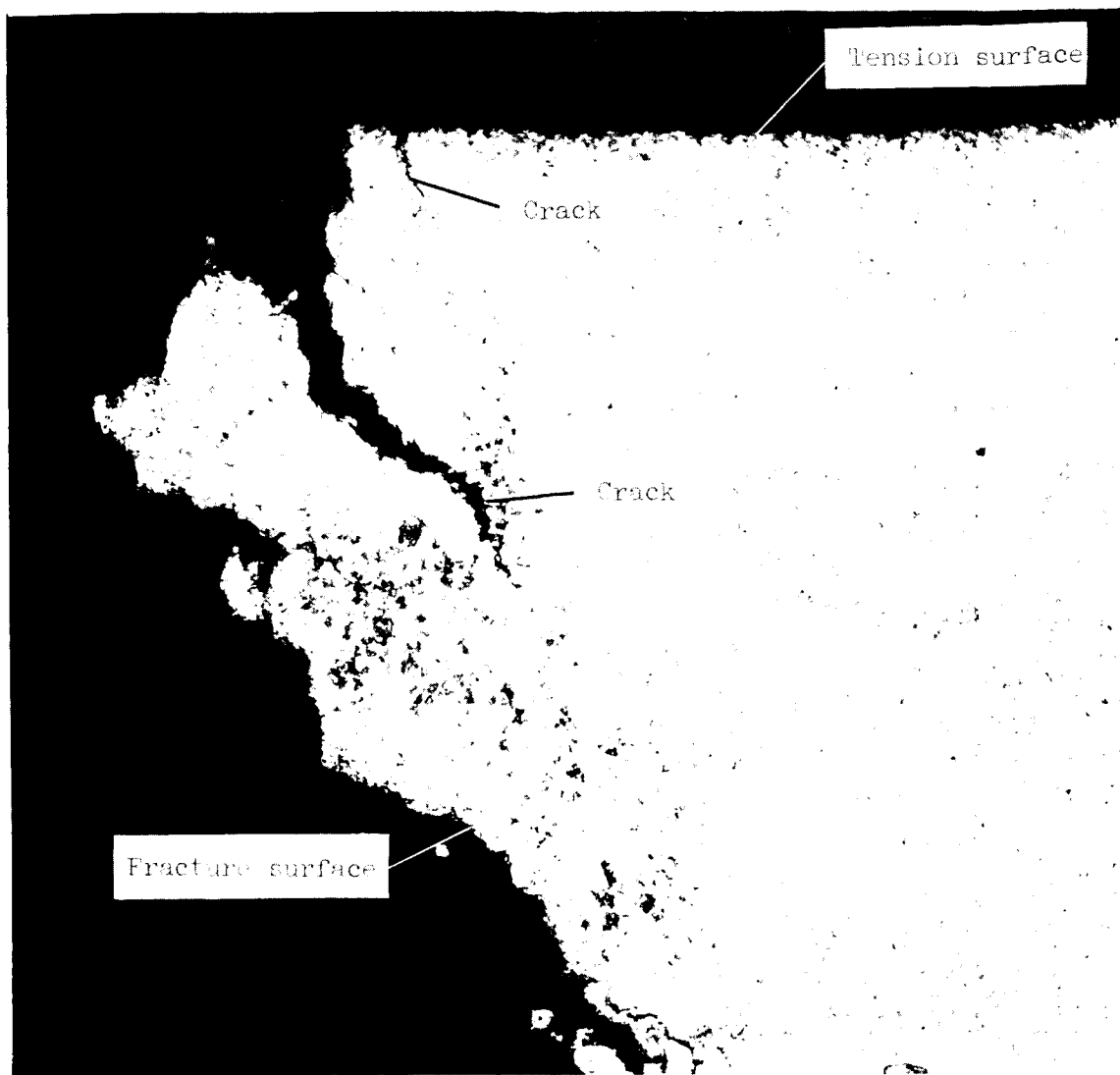550° F (561° K). ×500.

11

L-64-8383

Figure 8.- Edge view of stress corrosion cracks in fracture zone of
Ti-8Al-1Mo-1V specimen exposed in moist chlorine for 500 hours
at 550° F (561° K). x150.

(experiments 9, 6, 10, and 11 in table I). However, the thickness increased
during exposure at 550° F (561° K). The increase amounted to as much as
100 angstroms, as estimated by the color change of the surface, after
3000 hours exposure.

The results in figure 10 indicate that oxide films less than 600 ang-
stroms do not noticeably affect stress corrosion cracking in Ti-8Al-1Mo-1V
under the experimental conditions. However, data in reference 7 showed that a
thicker gray oxide film (estimated from ref. 5 to be greater than 1000 Å)
offered some protection against salt stress corrosion in Ti-6Al-4V exposed at
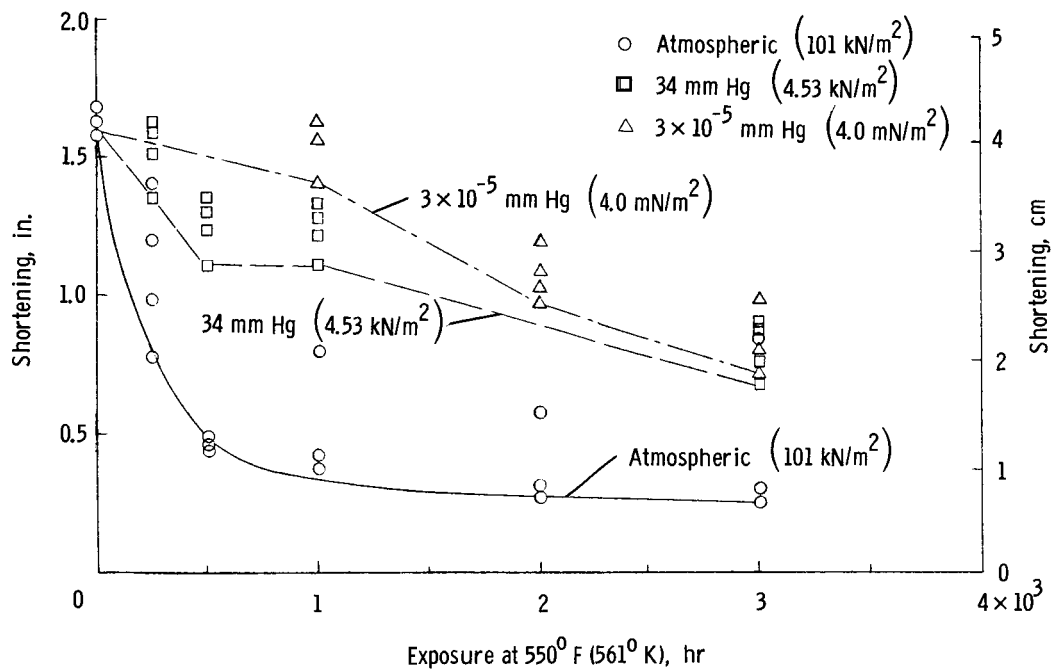750° F (672° K) and 800° F (700° K) up to 50 hours.

12

Figure 9.- Effect of pressure on shortening of salt-coated Ti-8Al-1Mo-1V specimens after exposure at 550° F (561° K).
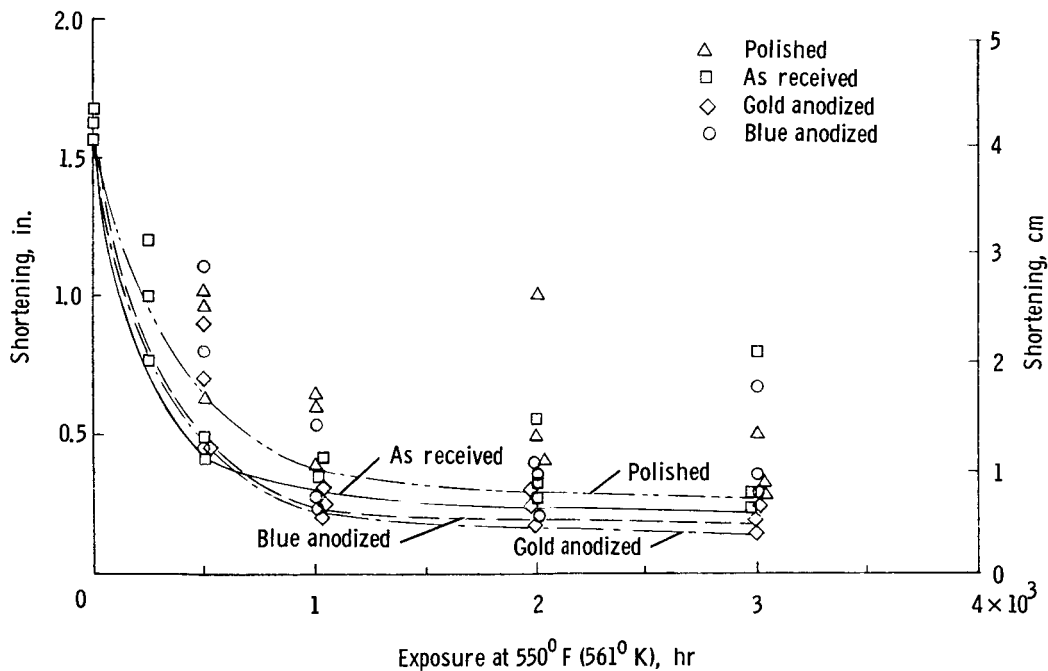

Figure 10.- Effect of different surface conditions on shortening of salt-coated Ti-8Al-1Mo-1V specimens after exposure at 550° F (561° K) in air.
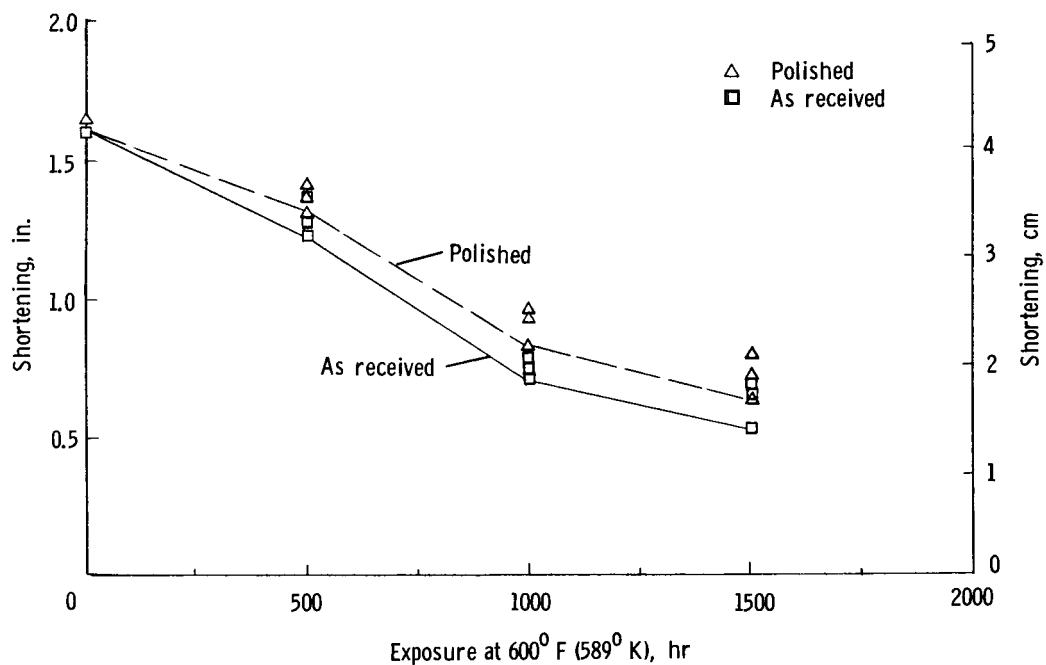
Figure 11.- Effect of surface condition at 3×10^{-5} mm Hg (4.0×10^{-3} mN/m^2) on shortening of salt-coated TI-8Al-1Mo-1V specimens after exposure at 600° F (589° K).
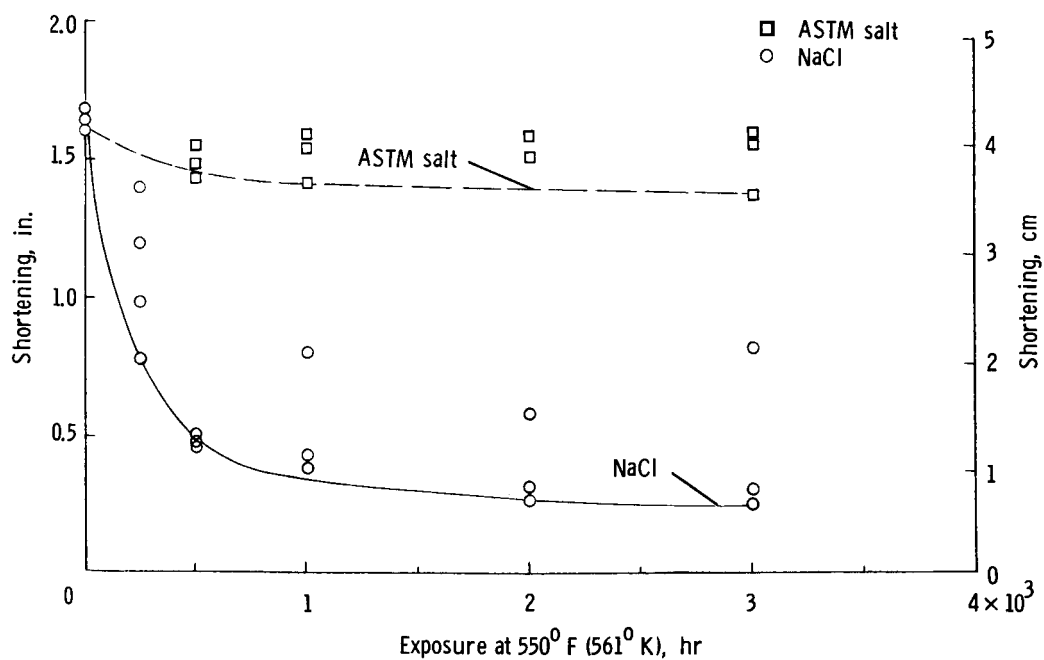

Figure 12.- Effect of salt composition on shortening of Ti-8Al-1Mo-1V specimens after exposure at 550° F (561° K).

14

As a further check on the effect of surface conditions, salt-coated specimens with polished and as-received surfaces were encapsulated separately under a pressure of 3×10^{-5} mm Hg (4.0 mN/m^2) (experiments 12 and 13 in table I). Each capsule was heated to 600° F (589° K) while pumping down to insure the removal of moisture. The results in figure 11 indicate that polished specimens demonstrated slightly better resistance to stress corrosion cracking than did the as-received specimens. However, because of the limited number of specimens tested, it was difficult to draw any definite conclusions as to the relative effects of these two surface conditions. These tests do show that very little gaseous oxygen or surface oxide is necessary to produce stress corrosion cracks in Ti-8Al-1Mo-1V at 600° F (589° K).

Effect of Salt Composition

The results for specimens with NaCl and ASTM salt coatings (experiments 6 and 14 in table I) are given in figure 12. For exposures up to 3000 hours at 550° F (561° K), the ASTM salt produced substantially less stress corrosion damage than the NaCl. This result was surprising since data from several investigations, such as reference 1, indicated that the effect of ASTM salt is probably more severe than that of NaCl. There seems to be no obvious explanation for this apparent inconsistency at this time. Additional stress corrosion tests are underway to determine the relative effects of NaCl, ASTM salt, and natural sea salt.

Identification of Corrosion Products

The X-ray diffraction patterns taken on the first coupon indicated the definite formation of TiO_2 (rutile) with possible traces of TiO. In addition, eight peaks, with their corresponding d-spacings and relative intensity values, were observed to be quite close to those listed by the ASTM index for $TiCl_2$. (See table II.) Absolute identification of $TiCl_2$ was difficult because four peaks, including one with a 60-percent relative intensity were missing completely, and three peaks are located at values of 2θ where they would be obscured by higher intensity Ti and TiO_2 peaks. Two further observations, however, lend evidence that $TiCl_2$ was actually formed with NaCl and titanium at 1000° F (811° K) and produced the eight peaks mentioned. First, when the corrosion products were dissolved in water, a gas bubbled off and the solution became slightly acidic. Kochka and Peterson (ref. 6) also observed this phenomenon and believed the following reactions occurred:

$$TiCl_2 + (x + 1)H_2O = TiO \cdot xH_2O + 2HCl$$

$$TiO + (x + 1)H_2O = TiO_2 \cdot xH_2O + H_2\uparrow$$
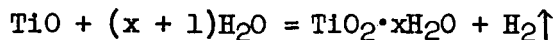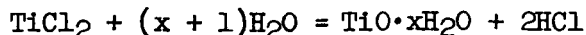
Second, the peaks identified as $TiCl_2$ decreased with time at room temperature and disappeared after the sample was washed in water. This would be expected since $TiCl_2$ is hygroscopic and decomposes in water.

TABLE II.- X-RAY DIFFRACTION ANALYSIS OF $TiCl_2$

| Experimental results		ASTM index	
d-spacing, $\overset{o}{A}$	Relative intensity	d-spacing, $\overset{o}{A}$	Relative intensity
2.6758	100	2.68	100
2.5060	25	2.51	20
2.3852	15	2.38	20
2.2607	10	2.27	20
Missing		2.14	60
Missing		2.03	10
Missing		1.95	40
1.8717	50	1.86	40
(a)		1.72	50
(a)		1.68	40
Missing		1.66	20
1.5276	25	1.53	40
(a)		1.44	40
1.1493	15	1.14	40
1.1128	10	1.11	40

[a]Obscured by higher intensity Ti or TiO_2 peaks.

The results for the second salt-coated coupon were similar to those for the first except that the $TiCl_2$ peaks were much weaker. The peaks observed for the uncoated coupon, exposed to the same conditions as the coated coupons, were identified as those of Ti and TiO_2. The salt-coated coupons were covered with gray, black, and yellow corrosion products, whereas the uncoated coupon exhibited the typical gray color of TiO_2.

Many investigators have proposed theories of the mechanism of stress corrosion cracking in titanium alloys where $TiCl_2$ is a corrosion product that is oxidized to form Cl_2 gas as follows:

$$TiCl_2 + O_2 \rightarrow TiO_2 + Cl_2\uparrow$$
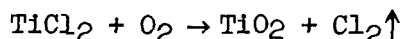
The chlorine then reacts with the titanium metal, which in turn initiates stress corrosion cracks and forms more $TiCl_2$ to repeat the cycle:
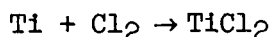
$$Ti + Cl_2 \rightarrow TiCl_2$$

The difficulty in verifying this mechanism has been in identifying the $TiCl_2$. The results presented in reference 9 include picking up the three strongest X-ray diffraction lines of $TiCl_2$ by using a molten-salt bath to produce the corrosion product.

In this experiment, at least 15 other peaks were observed that could not be identified even though several peaks corresponded to those for different titanium oxides and sodium titanates. More work needs to be done in order to identify these peaks and more data are needed for positive identification of $TiCl_2$ as one of the main reaction products. Future work will include the use of a furnace attachment which permits X-ray diffraction of corrosion products while they form at elevated temperature.

CONCLUDING REMARKS

The effect of various environmental factors on the salt stress corrosion of Ti-8Al-1Mo-1V titanium-alloy sheet (duplex annealed) at 550° F (561° K) and 600° F (589° K) was investigated in an attempt to learn more about the nature of this phenomenon. Stress corrosion damage was lessened by reducing the oxygen content or lowering the pressure of the environment. Air with dewpoints of -40° F (233° K) and 60° F (289° K) and thin oxide films with thicknesses less than 600 angstroms had little effect on stress corrosion cracking. Moist chlorine caused severe stress corrosion failure within 500 hours at 550° F (561° K) and appears to form a $TiCl_3$ corrosion product. NaCl produced considerably more stress corrosion damage than ASTM salt (six parts NaCl to one part $MgCl_2$, by weight) for exposure up to 3000 hours. $TiCl_2$ appears to be one of the important corrosion products produced with NaCl and Ti-8Al-1Mo-1V at 1000° F (811° K) and may be the key product involved in the salt stress corrosion mechanism at 550° F (561° K) and 600° F (589° K).

Langley Research Center,
    National Aeronautics and Space Administration,
        Langley Station, Hampton, Va., October 9, 1964.

APPENDIX A

CONVERSION OF U.S. CUSTOMARY UNITS TO SI UNITS

The International System of Units (SI) was adopted by the Eleventh General Conference on Weights and Measures, Paris, October 1960, in Resolution No. 12 (ref. 3). Conversion factors required for units used herein are:

Length: Inches $\times$ 2.54 = Centimeters (cm)
Feet $\times$ 0.3048 = Meters (m)

Force: Pounds $\times$ 4.448 = Newtons (N)

Stress: Kips per square inch (ksi) $\times$ 6.894 = Meganewtons per square meter (MN/m^2)

Temperature: $\frac{5}{9}(^\circ F + 459.67) = {}^\circ K$

Pressure: mm Hg $\times$ 133.32 = Newtons per square meter (N/m^2)
Atmospheres $\times$ 1.013 $\times$ 10^5 = Newtons per square meter (N/m^2)

Volume: Gallons $\times$ 3.79 $\times$ 10^{-3} = Cubic meters (m^3)

Mass: Ounces $\times$ 2.83 $\times$ 10^{-2} = Kilograms (kg)

Prefixes to indicate multiples of units are:

mega (M) 10^6

kilo (k) 10^3

centi (c) 10^{-2}

milli (m) 10^{-3}

18

APPENDIX B

ANODIZING PROCEDURE

The procedure used to anodize the Ti-8Al-1Mo-1V specimens electrochemically was as follows:

(1) Pretreatment:

      (a) Pickle 30 seconds in solution of 35 percent HNO_3 and 3 percent HF, by volume

      (b) Wash thoroughly in distilled water

      (c) Agitate in methyl alcohol

      (d) Remove alcohol immediately with warm air blast

      (e) Anodize immediately

(2) Electrolyte:

    Saturated $NaNH_4HPO_4$ at room temperature

(3) Electrical settings:

    15 volts and 0.5 ampere

    Current density of 30 amps/ft^2 (323 A/m^2)

(4) Anodizing times (approximate):

    Gold film, 5 seconds

    Blue film, 10 seconds

APPENDIX C

ENCAPSULATION OF SPECIMENS

Specimens were encapsulated with different gaseous environments and reduced pressures in glass tubes as follows:

(1) Three or four salt-coated specimens were placed in a 1-inch- (2.54-cm-) diameter glass tube approximately 12 inches (30.5 cm) long.

(2) Glass wool was packed around the ends of the specimens to prevent spalling of the salt coating due to handling.

(3) Both ends of the tube were drawn down to approximately 1/8 inch (0.3 cm) by using a glass lathe and an oxypropane torch to provide an inlet and outlet for the desired gas. (See fig. 2(a).) To obtain a reduced pressure capsule, one end was sealed off and the other necked as shown in figure 2(b).

(4) The tubes were purged with the desired gas for at least 1/4 hour and then sealed quickly. The outlet was sealed first to prevent any entrance of outside air. The reduced-pressure capsules were pumped down to the desired pressure by use of a portable pumping system consisting of a mechanical pump and a 2-inch (5.08-cm) diffusion pump. A flexible, thick-walled plastic hose and clamps were used to connect the capsule to the pumping system. The capsule was placed in a small ceramic tube furnace when an encapsulation at elevated temperature was desired. A capsule, which has been sealed off and is ready for exposure, is shown in figure 2(c).

REFERENCES

1. Martin, George (With appendix A by L. Lackman and R. M. Ault): Long Term
   Stress Corrosion Tests at Elevated Temperature (Third Interim Report).
   Rept. No. TFD 62-1175, North Am. Aviation, Inc., Sept. 14, 1962.

2. Braski, David N.; and Heimerl, George J.: The Relative Susceptibility of
   Four Commercial Titanium Alloys to Salt Stress Corrosion at 550° F. NASA
   TN D-2011, 1963.

3. Anon.: International System of Units, Resolution No. 12. NASA TT F-200,
   1964.

4. Andreeva, V. V.: Behavior and Nature of Thin Oxide Films on Some Metals in
   Gaseous Media and in Electrolyte Solutions. Corrosion, vol. 20, no. 22,
   Feb. 1964, pp. 35t-46t.

5. Anderson, A. A.; Menard, R. C.; Rittenhouse, D.; and Roepke, W. W.: Optical
   Measurement of Oxide Thickness of Titanium. ARL 32, U.S. Air Force,
   May 1961.

6. Kochka, E. L.; Petersen, V. C.: The Salt Corrosion of Titanium Alloys at
   Elevated Temperatures. Final Tech Rept. (Contract No. NOas 60-6004-c),
   Crucible Steel Co. of Am., Jan. 15, 1961.

7. Mallory-Sharon Titanium Corp.; Pratt & Whitney Aircraft; et al.: Progress
   Report on the Salt Corrosion of Titanium Alloys at Elevated Temperature
   and Stress. TML Rept. No. 88 (Contract No. AF 18(600)-1375), Battelle
   Mem. Inst., Nov. 20, 1957.

8. Early, F. R.; and Covington, L. C.: Investigation of the Mechanism of Stress
   Corrosion of Ti-5Al-2.5Sn Alloy Exposed to Hot Salt Conditions. Progr.
   Rept. No. 19, Titanium Metals Corp. of Am., Feb. 1964.

9. Crossley, Frank A.; Reichel, C. J.; and Simcoe, C. R.: The Determination
   of the Effects of Elevated Temperatures on the Stress Corrosion Behavior
   of Structural Materials. WADD Tech. Rept. 60-191, U.S. Air Force, May
   1960.